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NOVEL SOL-GEL DEPOSITION FOR REPAIR OF CONDUCTING PATH IN CONDUCTING PATHS IN POLYCERAMIC SYSTEMS

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The present project involves research and development of conducting polymer sol-gel composites for repair of conducting paths in polceramic systems. During Phase I, we developed and carried out the synthesis of processible conducting polymers and organic/inorganic hybrid sol-gel materials. Sol-gel composite materials prepared during Phase I have high electrical condcutivity (ca. 30 S/cm) and adhere strongly on the surface of ceramic materials. The conductivity of ITO glass was the same as its original value after repairing a crack with these sol-gel composites. Conductive sol-gel composites can be prepared with a very small amount of processible conducting polymers, ca. 3%. Composites with high concentration of conducting polymers (70% - 90%), however, showed better stability. Sol-gel metal oxides and conducting polymers are also ideal electrode materials for the fabrication of mutilayer capacitors and rechargeable batteries.

Upon completion of the present work, it is evident that the feasibility of the technology proposed for repairing conducting paths in polyceramic systems was demonstrated.

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SUMMARY

The present project involves research and development of conducting polymer/sol-gel (CP/sol-gel) composites for repair of conducting paths in polyceramic systems. We proposed to apply the novel idea of incorporating electrically conducting polymers into the sol-gel matrix to improve conductivity of the composites. Sol-gel metal oxides and conducting polymers are also ideal electrode materials for the fabrication of mutilayer capacitors and rechargeable batteries.

One of the major difficulties of preparing conductive composites using conducting polymers is doping of polymers after formation of the composite materials. This was overcome by using conducting polymers which were processible in the conductive form. During Phase I, we developed and carried out the synthesis of processible conducting polymers and organic/inorganic hybrid sol-gel materials. The ideal candidates for fabrication of conductive adhesives are polyanilines with suitable dopant ions.

Sol-gel composite materials prepared during Phase I have high electrical conductivity (ca. 30 S/cm) and adhere strongly on the surface of ceramic materials. In accordance with the effort outlined, a number of CP/sol-gel composites were successfully synthesized and evaluated. During Phase I, effects of (1) sample preparation procedure, (2) substituent on matrix polymer chain, (3) the concentration of conducting polymer, methylmethacrylate, and $Si(OEt)_4$, (4) aging and (5) solvent on the conductivity of the resulting CP/sol-gel composites were investigated. Conductive sol-gel composites can be prepared with a very small amount of processible conducting polymers, ca. 3%. Composites with high concentration of conducting polymers (70 % - 90 %), however, showed better stability. Thermal and mechanical properties of these composites were also studied by means of Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analyzer (DMA). Sol-gel composites containing polythiophene, and polypyrrole were also prepared and evaluated.

Our experimental results indicated that the copolymer containing 90% MMA and 10% MSMA provided better adhesive bonding and mechanical properties when compared with organic-inorganic hybrid materials. Since poly(butyl methacrylate) is a better film forming material than poly(methyl methacrylate), we also synthesized copolymers containing butyl methacrylate (BMA) for evaluation. A three-component copolymer containing 90% Methyl Methacrylate (MMA), 5% Butyl Methacrylate (BMA), and 5% 3-(trimethoxysilyl)propy Methacrylate (MSMA) provides superior adhesive bonds on ceramic surfaces after curing. The THF solution of this copolymer has a shelf lifetime of ca. one month.

Upon completion of the present work, it is evident that the feasibility of the technology proposed for repairing conducting paths in polyceramic systems was demonstrated. With suitable design, the conductivity and physical properties of CP/sol-gel composites could be further improved.

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I. INTRODUCTION

The present project involves research and development of conducting polymer/sol-gel (CP/sol-gel) composites for repair of conducting paths in polyceramic systems. The sol-gel processes have regained scientific and technological importance during the past decade. These processes offer new approaches to the preparation of homogeneous ceramic and glass at low temperature. On the other hand, conducting polymers are an emerging class of materials that possess the electrical properties of metals while retaining the mechanical properties and processibility of conventional polymers. We proposed to apply the novel idea of incorporating electrically conducting polymers into the sol-gel matrix to improve conductivity of the composites. Sol-gel metal oxides and conducting polymers are also ideal electrode materials for the fabrication of mutilayer capacitors and rechargeable batteries. The technical objectives as identified in the Phase I proposal were:

1. Synthesize inorganic and polymer-inorganic sol-gel materials and evaluate the processibility of the mixture.
2. Incorporate conducting polymers into sol-gel matrix to improve the conductivity of the composites.
3. Investigate the effects of substituents of conducting polymers and compositions of the sol-gel materials on the performance of the composites in repairing conductive paths in polyceramic systems.
4. Carry out theoretical modeling work on the sol-gel composite-polyceramic interfacial interactions in order to understand the bonding between sol-gel materials and substrate.

One of the major difficulties of preparing conductive composites using conducting polymers is doping of polymers after formation of the composite materials. This was overcome by using conducting polymers which were processible in the conductive form. During Phase I, we developed and carried out the synthesis of processible conducting polymers and organic/inorganic hybrid sol-gel materials. One-step chemical polymerization techniques were evaluated for scale-up production of conducting polymers. Conductive composites of these materials were also successfully prepared. We prepared conductive sol-gel composites with a very small amount of processible conducting polymers, < 5%. Composites with high concentration of conducting polymers (70 % - 90 %), however, showed better stability and higher conductivity. At present, the composites containing 70 % or higher concentration of polyaniline have conductivity in the range of 20 S/cm to 30 S/cm. This value is comparable with the conductivity of ITO glass. These composite coatings also strongly adhere to the glass substrate due to the interaction between matrix polymer and oxides on the polyceramic surface. We were not able to remove the coating using scotch tape.

During Phase I, effects of (1) sample preparation procedure, (2) substituent on matrix polymer chain, (3) the concentration of conducting polymer, methylmethacrylate, and $Si(OEt)_4$, (4) aging and (5) solvent on the conductivity of the resulting CP/sol-gel composites were investigated. Sol-gel composites containing polyaniline, polythiophene, and polypyrrole were evaluated. The conductivities of the composite materials are stable for at least two months when the concentration of conducting polymer was greater then 70 %. Thermal and

mechanical properties of these composites were also studied by means of Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analyzer (DMA).

Our experimental results indicated that the copolymer containing 90% MMA and 10% MSMA provided better adhesive bonding and mechanical properties when compared with organic-inorganic hybrid materials. Since poly(butyl methacrylate) is a better film forming material than poly(methyl methacrylate), we also synthesized copolymers containing butyl methacrylate (BMA) for evaluation. A three-component copolymer (MMA-BMA-MSMA) containing 90% MMA, 5% BMA, and 5% MSMA provides superior adhesive bonds on glass after curing. The copolymer is much more stable than the one containing 10% MSMA in air because there are less reactive sites.

II. EXPERIMENTAL

II.1 Synthesis of Conducting Polymers

One of the objectives of proposed work was to synthesize processible conducting polymers for fabrication of CP/sol-gel composites. During Phase I, sol-gel composites prepared from polyaniline (emeraldine base and emeraldine salt), polypyrrole and poly(3-methylthiophene) were prepared and evaluated. Conducting polymers were synthesized by the one-step chemical polymerization technique. Polyaniline was synthesized in aqueous solution using $(NH_4)_2S_2O_8$ as oxidant [1]. The delocalized electronic structures of conducting polymers tend to yield relatively stiff chains. Recently, this was overcome by substituting a proton with long linear alkyl hydrocarbon chains at the three position of the thiophene ring. Furthermore, the functionalized dopant ion also can induce processibility of conducting polymers [2]. Functionalized dopants were incorporated into polymer matrices during synthesis or by post polymerization doping processes.

Polypyrrole, polythiophene and poly(3-methylthiophene) were synthesized in acetonitrile using $FeCl_3$ as oxidant. The resulting polymers were characterized by means of elemental analysis, IR, UV-Vis, electroanalytical and spectroelectroanalytical techniques. Based on elemental analysis results, the doping level of chemically synthesized polyaniline and poly(diphenylamine) was in the range of 40 % to 50 % while the value is between 20 % and 30 % for the other polymers synthesized during Phase I. In the present case, the conductivities of substituted polyaniline were very low. Therefore, these polymers were not incorporated into sol-gel matrices for evaluation. Table I shows the typical conductivity of the resulting conducting polymers.

Table I. Conductivities of chemically synthesized conducting polymers.

	Conductivity
polyaniline	4 S/cm*
poly(o-toluidine)	10^{-1} S/cm
poly(ethylaniline)	10^{-3} S/cm
poly(diphenylamine)	10^{-2} S/cm
Polypyrrole	8 S/cm
polythiophene	6 S/cm
Poly(3-methylthiophene)	113 S/cm

* Conductivity of as synthesized emeraldine hydrochloride; Conductivity of polyaniline strongly depends on the solvent used for processing. The conductivity of polyaniline varies between 1 S/cm and 400 S/cm.

II.2 Synthesis of Sol-gel Materials

Copolymers of methylmethacrylate (MMA) and 3-(trimethoxysilyl)propyl methacrylate (MSMA) were synthesized by free-radical polymerization [3,4]. Syntheses of copolymers were carried out under an inert atmosphere (N_2) at 60°C using benzoyl peroxide (BPO) as initiator. For a typical copolymerization procedure, to a 250-ml three necked round bottom flask fitted with nitrogen inlet and outlet and a condenser was added a solution of 23.04 g (0.23 mole) MMA, 6.35 g (0.0265 mole) MSMA and 2.48 g (0.0102 mole) BPO in 64 ml dry benzene. The resulting polymers were obtained by precipitating in dry hexane. The resulting polymer contain 10 % MSMA and 90 % MMA. Copolymers with different compositions can be prepared by varying the molar ratio of the starting materials.

Hydrolysis and polycondensation of the copolymers and $Si(OEt)_4$ were carried out in the presence of acid (HCl) using THF, NMP, m-cresol or toluene as solvent. The reaction mixture turned to solid within three days. However, the resulting sol-gel material lost about 0.3% - 1% weight in a week. This suggests that the reaction may not be fully complete. The weight of the resulting sol-gel materials reached a steady value after about 2 weeks. Large size, ca. 4 cm^2 and 1 mm thick, transparent sol-gel hybrid materials can be obtained when THF is used as solvent. When toluene was used as solvent, the top portion of the reaction mixture turned to solid within three days while the bottom portion was still in the liquid state. This resulted in serious cracking in sol-gel glass. Finally, only small pieces of sol-gel materials were obtained and white colored material was observed in the bottom of the hybrid glass. The size of the resulting sol-gel glass also depends on the concentration of organic component. Large size sol-gel glass were obtained when the concentration of organic component is high. This is an indication that organic component could provide superior mechanical property to the novel conductive composites.

Although THF appears to be a good solvent for preparing thick sol-gel glass, this solvent may not be suitable for preparing sol-gel coatings. This solvent evaporates rapidly before completion of polymerization. Phase separation could occur in this case. The viscosity of solution increases in the later stage of polymerization. Thick solution, however, is not suitable for repairing small cracks in conducting path. The proper timing and use of mixed solvents or solvent with higher b.p. for preparing sol-gel coatings were investigated.

III. RESULTS AND DISCUSSION

III.1 Sol-gel Composites Prepared from Emeraldine Base

We have set up a collaboration with professor Wei's group of the Chemistry Department, Drexel University, for the preparation and characterization of composite materials. The NMP soluble portion of emeraldine base was blended with sol-gel reaction mixture in the same solvent. A copolymer containing 20% MSMA and 80% MMA was used for sample preparation. The solution was dried in a vacuum oven at 60°C until the gel was formed. The resulting sol-gel composites (polyaniline/poly(MMA-MSMA)-SiO_2) were doped with HCl aqueous solution to convert these materials to conductive state. The effects of polyaniline loading and the concentration of HCl on the conductivity of sol-gel glass are shown in Figure 1. The resistance of sol-gel composite was measured by two-point probe method using a FLUKE 8010A multimeter. This figure clearly indicates that the resistance of sol-gel glass decreases as polyaniline loading and the concentration of HCl increase. The concentration of polyaniline in the sol-gel materials was calculated based on the feed (ie. including the insoluble portion of emeraldine base). The actual content of polyaniline should be less than what is shown in Figure 1.

Electrical, mechanical and thermal properties of emeraldine hydrochloride (EHCl)/SiO_2 composites prepared by Dr. Wei's group were investigated. Figures 2 and 3 show the conductivity vs. %EB and modulus (E') vs %SiO_2 curves of the composite materials. The conductivity of composite films increased as conducting polymer loading increased. The storage modulus increased sharply as SiO_2 concentration increased to ca. 25 %. Further increase in the loading of SiO_2 resulted in a decrease of modulus. Figure 4 shows the glass transition temperature (T_g) and Tan delta of emeraldine base-SiO_2 composite films as a function of SiO_2 loading.

III.2 Sol-gel Composites Prepared from Conductive Polyaniline

In this section, we discuss the synthesis and properties of the composite materials prepared from polyaniline which is processible in the conductive form. The disadvantages of the technique described in section III.1 include: 1) acidic doping after formation of composites, and 2) use of high b.p. solvent. A technique was developed at Gumbs to prepare conductive sol-gel composites at room temperature. Soluble conductive polyanilines were used to synthesize conductive composites. Since these polymers are soluble in the conductive state in low b.p. solvent such as THF, Toluene and Xylene, doping of the resulting conducting polymer/sol-gel composites is not necessary.

Functionalized dopant ions, such as camphorsulfonic acid and dodecylbenzene sulfonic acid, can induce processibility of conducting polymers. Functionalized dopants were introduced into polyaniline matrix during polymerization as well as through post polymerization doping. The conductivity of as synthesized polymers containing functionalized dopant are ca. 1 S/cm which is the same as emeraldine hydrochloride. These polymers are soluble in common organic solvents, such as NMP, m-cresol, THF, and Xylene etc. The conductivity of a polymer coating strongly depends on the type of processing solvent. The surface resistance of

polyaniline film containing functionalized dopant prepared with NMP is ca. 17 $M\Omega/cm^2$ and it is ca. 115 Ω/cm^2 when m-cresol is used as solvent. Conductive composites of polyaniline, polypyrrole, and polythiophene were successfully prepared and evaluated. The resistance of a composite containing ca. 3.4 wt% polyaniline is in the range of 300 KΩ to 600 KΩ when THF was used as solvent. This is comparable to the lowest resistance obtained for the composites prepared from emeraldine base. However, the polyaniline content is much lower.

During Phase I, effects of (1) sample preparation procedure, (2) substituent on matrix polymer chain, (3) the concentration of conducting polymer, methylmethacrylate, and $Si(OEt)_4$, and (4) solvent on the conductivity of the resulting sol-gel/conducting polymer composites were investigated. The conductive surface of ITO glass was cut across with a diamond glass cutter to form an insulating path. Sol-gel reaction mixtures were then drop coated on scratches to make electrical contact between two ITO conductive surfaces. The resistance across the repaired conducting path was measured as a function of time. The distance between probes is 1 cm. Free standing films of conducting polymer/sol-gel composite were also prepared and evaluated.

III.2.1 Polyaniline/poly(MMA-MSMA)-SiO_2 composites

As a typical procedure for preparing sol-gel/conducting polymer composite, a solution of $Si(OEt)_4$ (TEOS) and small volume of HCl (a few drops) in THF was stirred for 30 minutes and then combined with a solution of copolymer and conducting polymer. The copolymer contains about 90 % MMA and 10 % MSMA. The compositions and conductivities of selected sol-gel composites are given in Tables II and III. Phase separation was observed when the reaction time for hydrolysis and polycondensation of TEOS was less than 30 minutes. The reaction time increased in the following order: sample #1 (ca. 13 minutes), #3, #4, #5 (ca. 30 minutes). For samples 2, 6 and 8, HCl was introduced into a mixture of copolymer, TEOS, and polyaniline in THF. The amount of white precipitates on composite coating decreased as the reaction time increased. The initial resistances of composite films which showed phase separation were slightly lower than those with longer TEOS reaction time. Cracking on those composite films (samples 1,2,3,4, and 8) occurred after about 2 weeks and resistance sharply increased (ca. 1 to 2 order magnitude). Figure 5 clearly demonstrates the effects of synthesis procedure on the quality of composite film. Compositions of composite coatings #3 and #5 are about the same. The reaction time for TEOS was 20 and 30 minutes, respectively.

Table II. Compositions and conductivities of sol-gel composites.

Sample	MMA-MSMA	TEOS	Polyaniline	Resistance 1 day	Resistance 60 days
1	23.3%	72.8%	3.9%	15.5 KΩ	126.8 KΩ
2	23.3%	73.4%	3.3%	7,780 KΩ	>30,000 KΩ
3	23.2%	72.9%	3.9%	25.7 KΩ	2,458 KΩ
4	23.2%	73.0%	3.9%	28.1 KΩ	323 KΩ
5	22.3%	73.7%	4.0%	6.3 KΩ	26.9 KΩ
6	69.3%	0 %	30.7%	-	-
7	83.2%	0 %	16.8%	33.0 KΩ	18.3 KΩ
8	14.3%	80.7%	5.1%	20.7 KΩ	4,380 KΩ

Cracking on composite films occurred at about the same time that the sol-gel reaction was completed. Figure 6 shows the weight lost vs. time curves for samples 5,6,7, and 8. The initial weight of sample was taken four days after mixing. The initial sol-gel reaction rate was speeded up if HCl was introduced to reaction mixture instead of adding the catalyst into TEOS solution and then mixing with copolymer solution.

Figure 7 shows the effects of conducting polymer, polyaniline, loading on the conductivity of sol-gel composites. For this study, 0.12 mmole HCl was added to 11.4 mmole TEOS in THF. The solution was stirred for 30 minutes and then combined with a THF solution of copolymer and polyaniline. The resistance of composite decreased as the concentration of polyaniline increased. Although polyaniline is quite stable in the laboratory environment, a gradual increase in resistance of sol-gel/conducting polymer composites was observed for polymer loading less than ca. 5%. The conducting polymer may interact with the sol-gel reaction products, resulting in dedoping of conducting polymer. One order magnitude increase in resistance of composite containing 3.2% polyaniline was observed after 2 months while the conductivity change was relatively small for composites with higher conducting polymer loading.

Table III. Compositions and conductivities of sol-gel composites.

Sample	MMA-MSMA	TEOS	Polyaniline	Resistance 1 day	Resistance 68 days
9	23.6%	73.2%	3.2%	550 KΩ	2,028 KΩ
10	23.1%	71.0%	5.9%	14 KΩ	91 KΩ
11	22.5%	68.8%	8.7%	0.9 KΩ	2 KΩ

Additional samples with the same compositions as samples 5 and 7 were prepared. For one of these samples, copolymer of MMA and MSMA was dissolved in toluene before mixing with other components. Use of the solvent appeared not to improve the physical properties of the resulting composites.

III.2.2 Polyaniline/poly(MMA-MSMA) composites

The results of previous experiments indicate that small amount of silicon oxide component could provide adhesive bonding between polyceramic substrate and conductive composite coating. High concentration of SiO_2, however, could result in cracking of the film or phase separation. The conductivity of composites can be further improved by increasing conducting polymer loading and improving processibility of conducting polymer and techniques for the fabrication of composites.

Polyaniline films with very high conductivity, 200 - 400 S/cm, can be prepared by using m-cresol as solvent. During Phase I, we also evaluated this solvent for the fabrication of conductive composites. Table IV lists the compositions and conductivity of polyaniline/sol-gel composite materials. The copolymer of MMA and MSMA (10%) was found to be soluble in m-cresol. Doped polyaniline or blends of emeraldine base and camphorsulfonic acid were dissolved in m-cresol and then a desired quantity of MMA-MSMA copolymer was added to the solution. When the content of copolymer was greater than 30 %, a small amount of THF was introduced to the mixture in order to lower the viscosity. We also evaluated camphoric acid as a doping material for polyaniline. However, the conductivity of resulting conducting polymer (sample #18) was lower than that containing camphorsulfonic acid.

Table IV. Compositions and conductivities of sol-gel composites.

Sample	MMA-MSMA	doping[a]	Polyaniline[b]	Resistance 1 day	Resistance 75 days
12	0 %	in-situ	100 %	24.6 Ω	22.3 Ω
13	9 %	in-situ	91 %	25.8 Ω	23.9 Ω
14	30 %	in-situ	70 %	32.6 Ω	33.7 Ω
15	0 %	post	100 %	32.6 Ω	36.0 Ω
16	12 %	post	88 %	30.7 Ω	30.2 Ω
17	38 %	post	62 %	33.8 Ω	35.4 Ω
18	0 %	post	100 %	353 KΩ	349 KΩ

a. in-situ: doping during polymerization;
post : post polymerization doping;
For sample 18, camphoric acid was used as doping material.
b. % doped polyaniline for samples 12, 13 and 14;
% emeraldine base for samples 15, 16 and 17.

Very high conductivity was obtained for sol-gel composites when the concentration of conducting polymer was greater than ca. 70% and m-cresol was used as solvent. The conductivity of an ITO glass was the same as its original value after repairing with these sol-gel composites. The typical resistance for an ITO glass measured by 2-probe technique was 33 $\pm$ 1 Ω. The probe distance was 1 cm. These materials also formed very strong adhesive bond to the surface of ITO glass. We were not able to remove the composite coatings on ITO glass using scotch tape. As shown in Figures 8 and 9, aging time has very little or no

effects on the conductivity of these composite materials. The stable reading of conductivity value indicates that the composite materials are chemically inert and also strongly adhere to the ceramic substrate. The resistance will sharply increase when there are cracks on composite coating or the coating separates from substrate.

In order to improve the performance of CP/sol-gel composite coatings, duplicate samples were prepared and evaluated at Drexel University. First, the effect of molar ratio of polyaniline and camphorsulfonic acid (CAS) on the conductivity of the resulting film was investigated. As shown in Table V, the conductivity of polymer film increased as the molar ratio (CAS/N) decreased from 1.5 to 0.5. For samples 15, 16 and 17, the molar ratio of CAS and nitrogen atom on polymer chain (CAS/N) is 1. The effect of polymer concentration on the conductivity of the resulting films was also investigated. The results are given in Table VI.

Table V. The effect of the molar ratio of CAS/N on the conductivity of polymer film.

Sample	EB (g)	CSA (g)	CSA/N	m-cresol (g)	Conductivity (S/cm)
19	0.04	0.051	1/2	4.0	112
20	0.04	0.117	5/4	4.0	48
21	0.04	0.143	3/2	4.0	31

Table VI. The effect of polyaniline concentration on the conductivities of polymer films.

Sample	EB (g)	CSA (g)	CSA/N	m-cresol (g)	Conductivity (S/cm)
19	0.04	0.051	1/2	4.0	112
22	0.08	0.102	1/2	4.0	27
23	0.16	0.205	1/2	4.0	7

A mixture of emeraldine base and camphorsulfonic acid with CAS/N ratio of 1/2 was then used to prepare conductive sol-gel composites. Figure 10 shows the effect of polyaniline concentration on the conductivity of the sol-gel composite materials and the composition of these materials are given in Table VII. The composite coatings were dried in air for three days without heat treatment. The copolymer contains 20 % MSMA and 80 % MMA.

Table VII. The compositions of conductivities sol-gel composites.

Sample	CSA-EB (g)	Copolymer (g)	m-cresol (g)	Conductivity (S/cm)
24	0.091	0.000	4.0	112.0
25	0.091	0.010	4.0	16.9
26	0.091	0.023	4.0	6.7
27	0.091	0.039	4.0	3.4
28	0.091	0.091	4.0	2.5
29	0.091	0.136	4.0	0.3

Thermal properties of these composite materials were investigated by means of DSC and TGA. Figures 11 and 12 show the DSC and TGA thermograms of a sol-gel composite material containing 70 % of polyaniline-CAS. Similar DSC thermograms were obtained for composite materials containing 40 % to 90 % polyaniline-CSA. We did not observed any clear thermal transition at temperatures below 200°C from DSC thermograms. The endothermic transition occurred at around 200°C was due to evaporation of m-cresol. Based on TGA thermogram, there was a large amount of m-cresol remaining in the composite films. It was found that the solvent has great effect on the conductivity of polyaniline. As shown in Figure 13, the conductivities of composite films decreased upon heat treatment. These samples were dried with an IR lamp.

III.2.3 Polyaniline/poly(MMA-MSMA-BMA) composites

Conductive composites containing organic-inorganic hybrid matrices were also prepared and evaluated. Phase separation was observed when the composite coatings were prepared with high concentrations of TEOS. The resulting coatings had poor mechanical properties. Cracks were found on these coatings after drying. Our experimental results indicated that copolymer containing 90% MMA and 10% MSMA provided better adhesive bonding and mechanical properties when compared with organic-inorganic hybrid materials. The organosilane functional groups of a composite coating react with OH groups on ITO substrate to form a covalent linkage. This reaction improves the stability of conductive composites. With an excess of organosilane groups, a reactive silanol group can also condense with other silanol groups on the polymer matrices. The resulting composite coatings became brittle. Since poly(butyl methacrylate) is a better film forming material than poly(methyl methacrylate), we also synthesized copolymers containing butyl methacrylate (BMA) for evaluation. A three-component copolymer (MMA-BMA-MSMA) containing 90% MMA, 5% BMA, and 5% MSMA provides superior adhesive bonds on glass after curing. The copolymer is much more stable than the one containing 10% MSMA in air because there are less reactive sites.

Figures 14 and 15 show the conductivity of polyaniline/sol-gel composites on micro slide and on ITO glass, respectively. The compositions of the sol-gel composites are given in Table VIII. The conductivity of composite coatings increased as the concentration of polyaniline loading increased. For repairing

ITO glass, we need about 70 % polyaniline.

Table VIII. Compositions and conductivities of sol-gel composites.

Sample	MMA-BMA-MSMA	Polyaniline	conductivity	Resistance
30	70 %	30 %	0.1 S/cm	104.9 Ω
31	50 %	50 %	0.7 S/cm	61.1 Ω
32	30 %	70 %	19.5 S/cm	42.1 Ω
33	10 %	90 %	27.8 S/cm	34.3 Ω

III.3 Sol-gel Composites Prepared from Other Conducting Polymers

Sol-gel composites of polypyrrole, polythiophene and poly(3-methylthiophene) were also prepared and evaluated. These conducting polymers are not soluble in any solvents. The polymer particles were suspended in a solution of sol-gel copolymer. Table IX lists the typical resistance of these composite coating on ITO glass. Although the conductivity of as synthesized poly(3-methylthiophene) was about two orders of magnitude higher than that of polyaniline, its sol-gel composite was not very conductive.

Table IX. Conductivities of conducting polymer/sol-gel composites.

Conducting Polymer	Sol-gel matrix	% Conducting Polymer	Resistance (Ω)
PPy	MMA-MSMA	77 %	13,990
PPy	MMA-BMA-MSMA	90 %	13,662
PT	MMA-BMA-MSMA	90 %	591
P3MT	MMA-BMA-MSMA	90 %	140,675

IV. CONCLUSIONS AND RECOMMENDATIONS

An assessment of conducting polymer/sol-gel ceramic composites as conductive adhesive materials for repairing conducting paths in polyceramic systems has been made. In accordance with the effort outlined, a number of CP/sol-gel composites were synthesized and evaluated. The following could be concluded upon completion of the present work:

1. Conducting polymer/sol-gel ceramic (CP/sol-gel) composites prepared during Phase I have high electrical conductivity (ca. 30 S/cm) and adhere strongly on the surface of ceramic materials.

2. Processible conducting polymers were successfully synthesized. Use of processible conducting polymers for the fabrication of sol-gel composites eliminates the difficulties of doping of polymer after formation of the composites.

3. The ideal candidates for fabrication of conductive adhesives are polyanilines with suitable dopant ions.

4. Conductive sol-gel composites can be prepared with very small amount of processible conducting polymers, ca. 3%. Composites with high concentration of conducting polymers (70 % - 90 %), however, showed better stability.

5. The conductivities of CP/sol-gel composites are proportional to the loading of conducting polymer and reach the maximum value in the concentration range of 70 % to 90 %.

6. A three-component copolymer containing 90% Methyl Methacrylate (MMA), 5% Butyl Methacrylate (BMA), and 5% 3-(trimethoxysilyl)propy Methacrylate (MSMA) provides superior adhesive bonds on ceramic surfaces after curing. The THF solution of this copolymer has a shelf lifetime of ca. one month.

7. The conductivity of ITO glass was the same as its original value after repairing a crack with these sol-gel composites.

From the above, it is evident that the feasibility of the technology proposed for repairing conducting paths in polyceramic systems was demonstrated. With suitable design, the conductivity and physical properties of CP/sol-gel composites could be further improved.

V. REFERENCES

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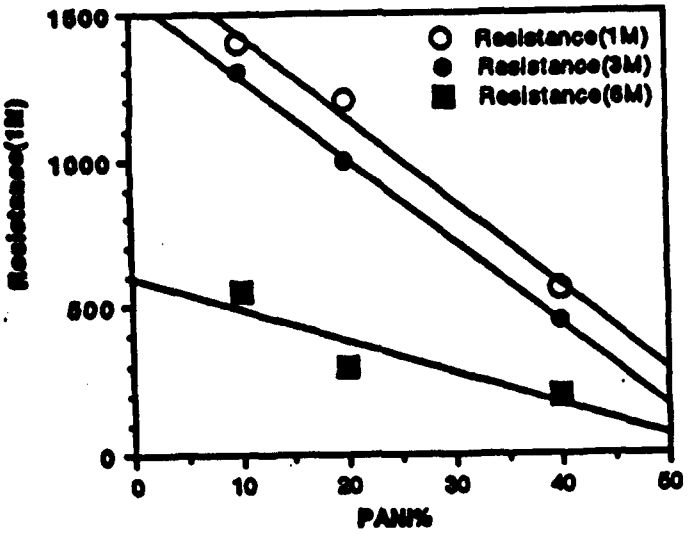

Figure 1. The effects of polyaniline content and [HCl] on resistance of polyaniline/poly(MMA-MSMA)-SiO_2.

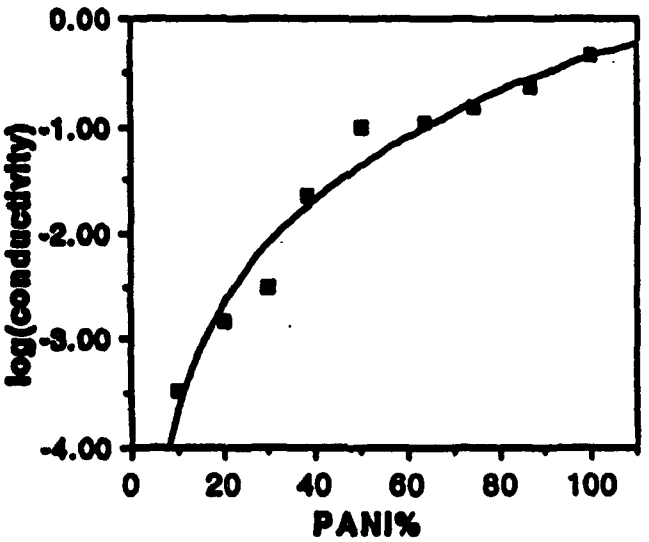

Figure 2. Conductivity vs %EB curve of EHCl/SiO_2 composites.

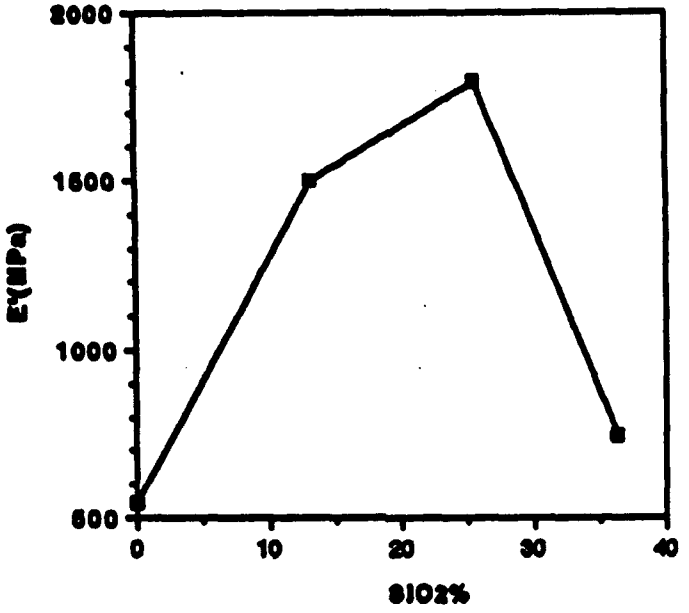

Figure 3. Mechanical properties vs %SiO_2 of EHCl/SiO_2 composites.

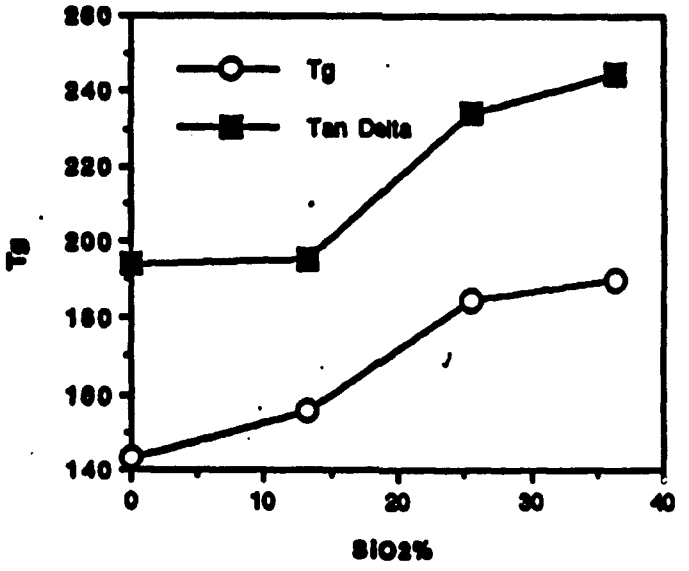

Figure 4. The glass transition temperature and Tan delta of emeraldine base-SiO_2 composite films as a function of SiO_2 loading.

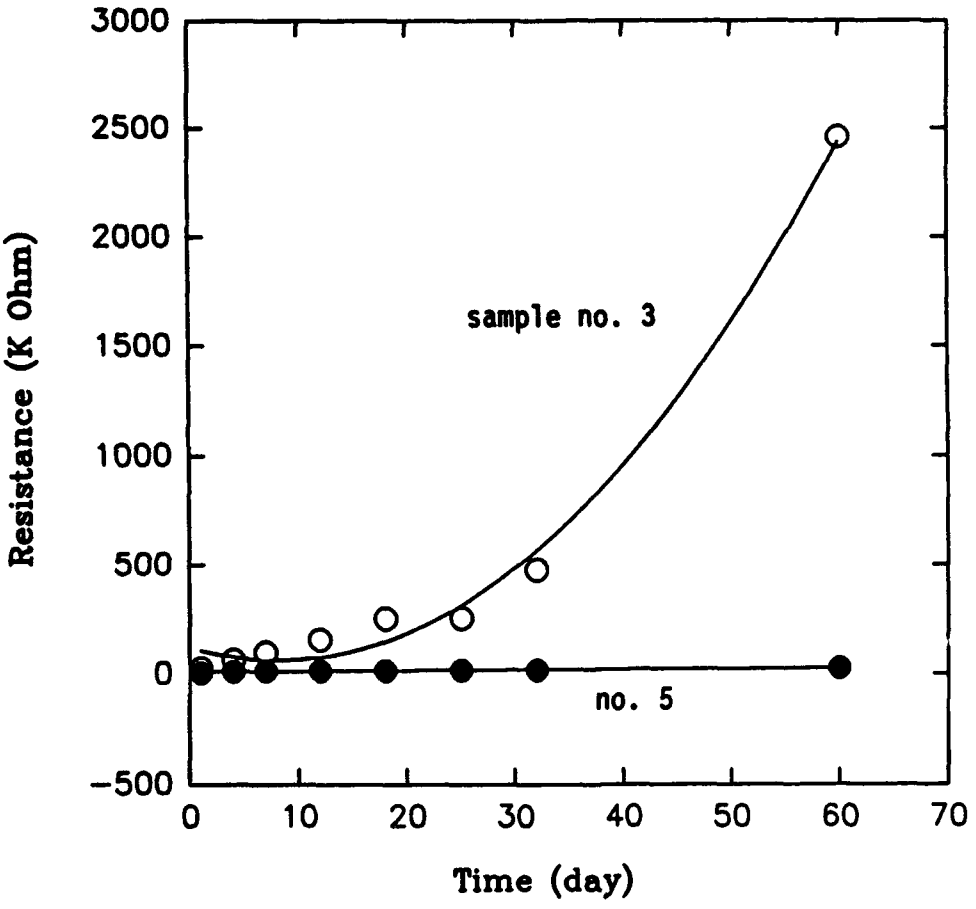

Figure. The effects of synthesis procedure on the quality of composite films.

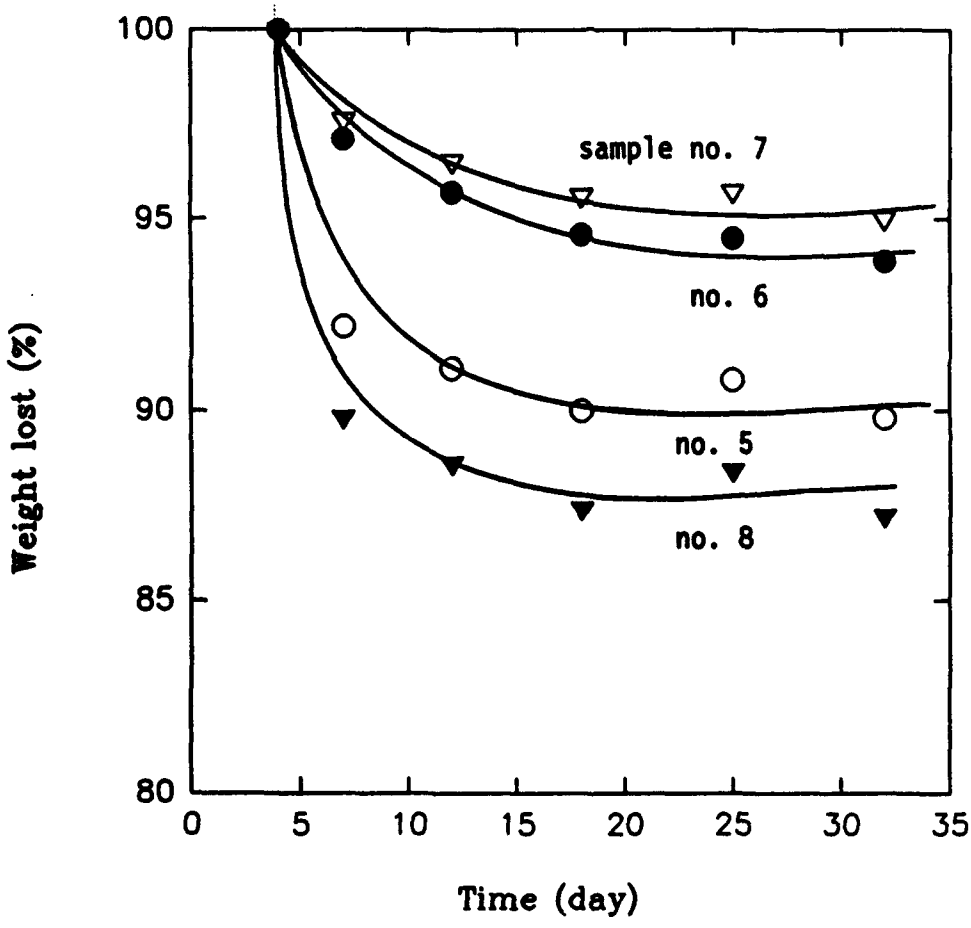

Figure 6. Weight lost vs time curves of polyaniline/ poly(MMA-MSMA)-SiO_2.

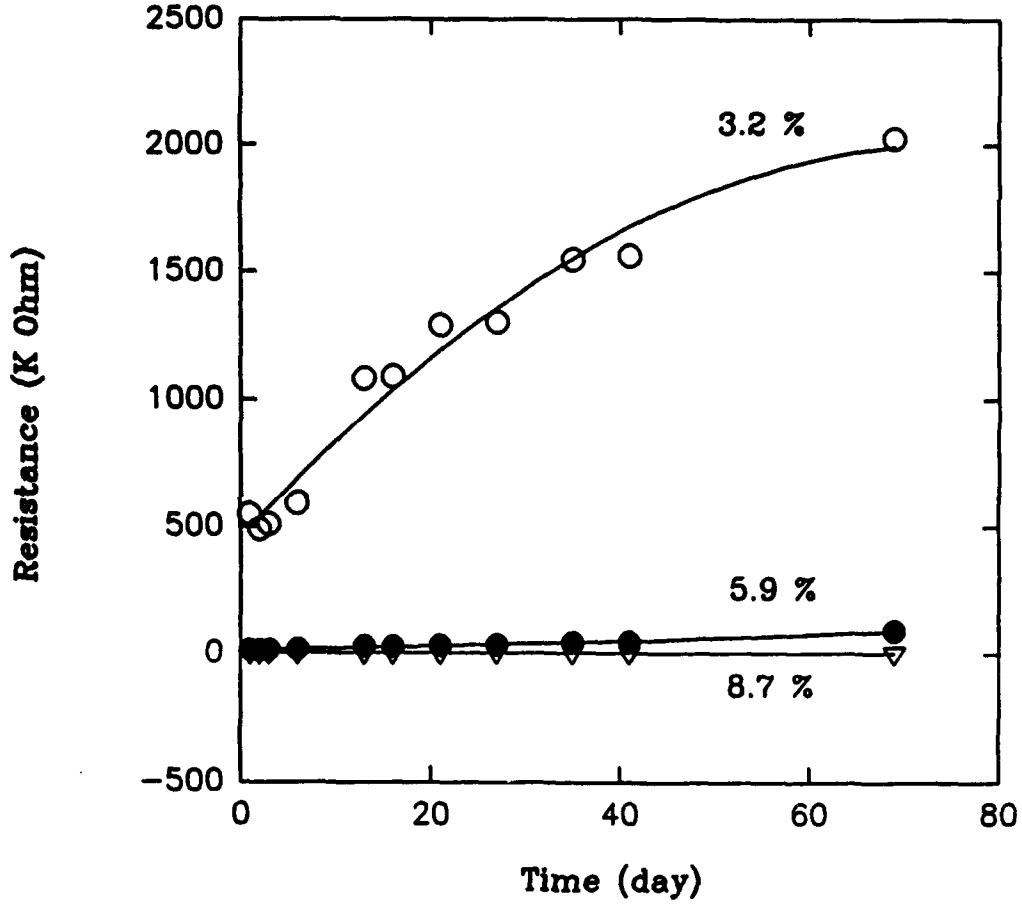

Figure 7. The effects of polyaniline loading on the conductivities of polyaniline/poly(MMA-MSMA)-SiO_2 composites.

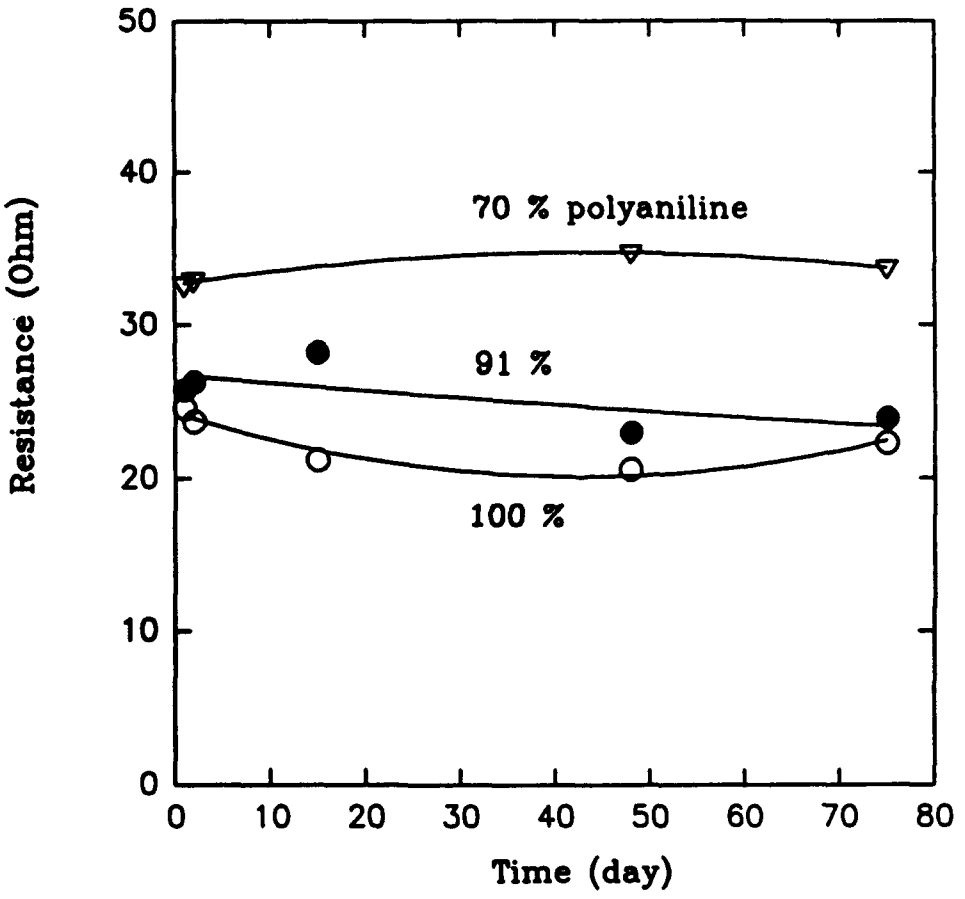

Figure 8. Resistance vs time curves of polyaniline (in-situ)/ poly(MMA-MSMA).

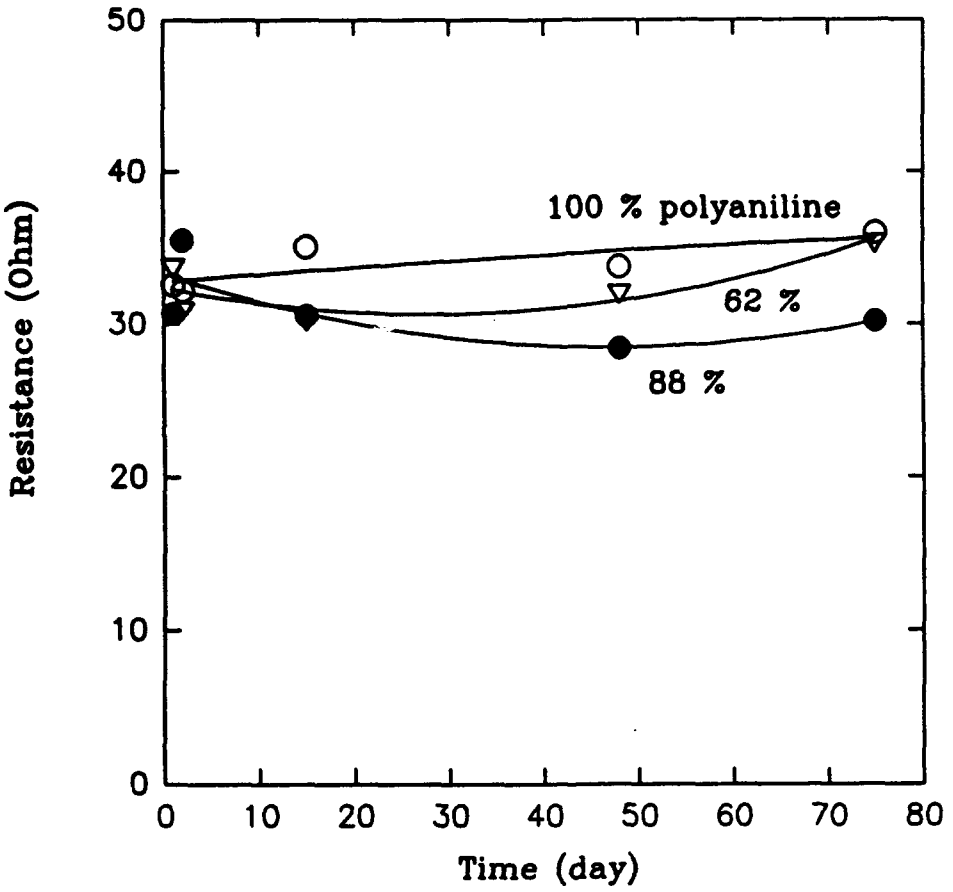

Figure 9. Resistance vs time curves of polyaniline (post)/ poly(MMA-MSMA).

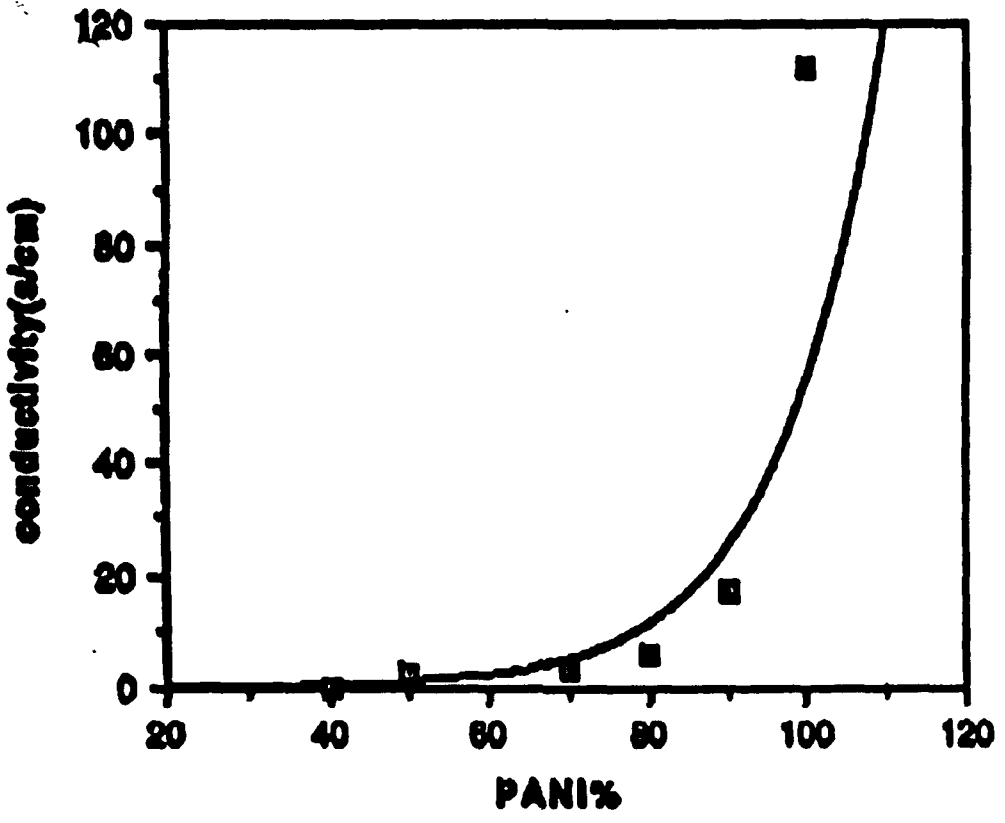

Figure 10. The effects of polyaniline concentration on the conductivities of polyaniline/poly(MMA-MSMA) composites.

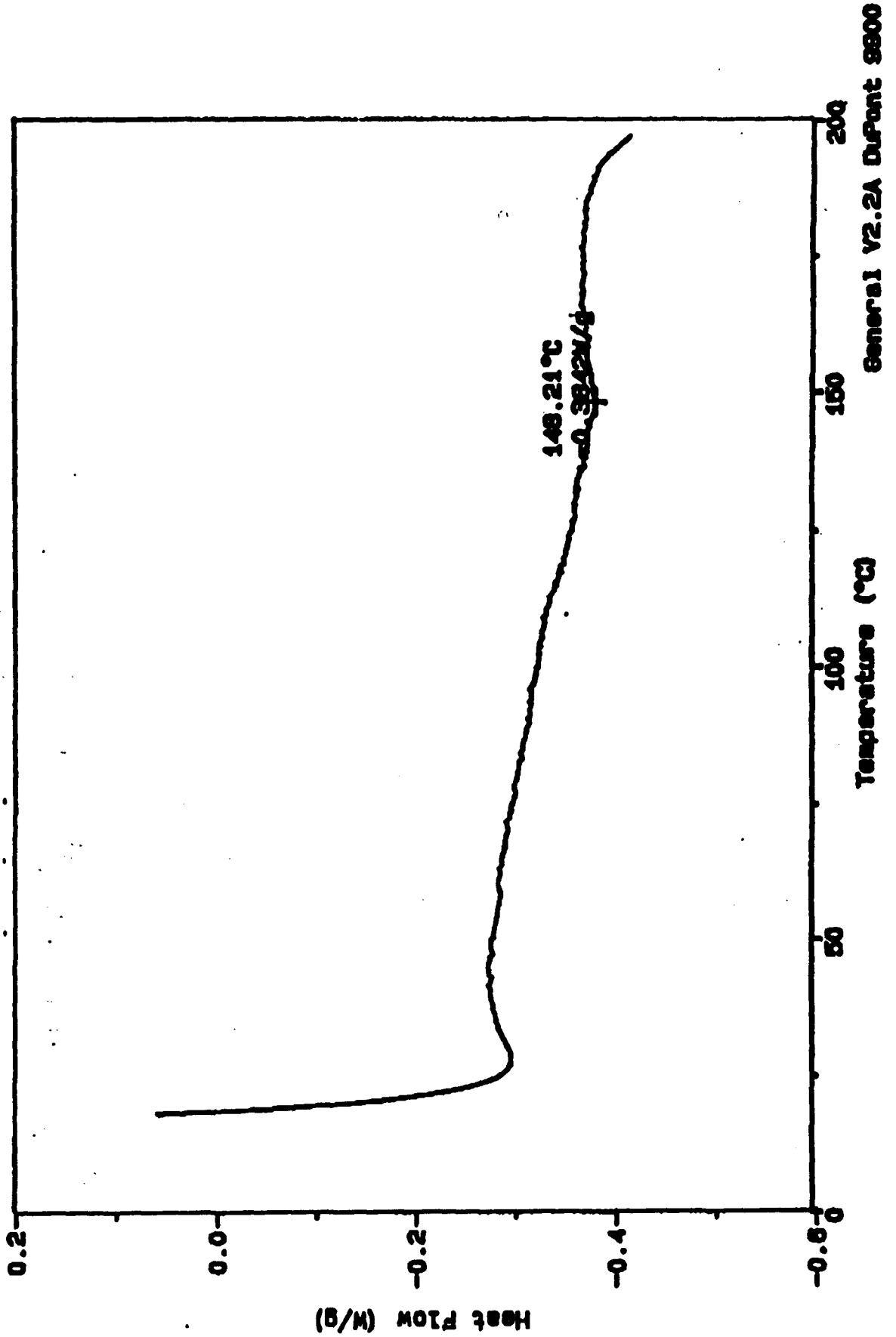

Figure 11. DSC thermogram of polyaniline (70%)/poly(MMA-MSMA) composite.

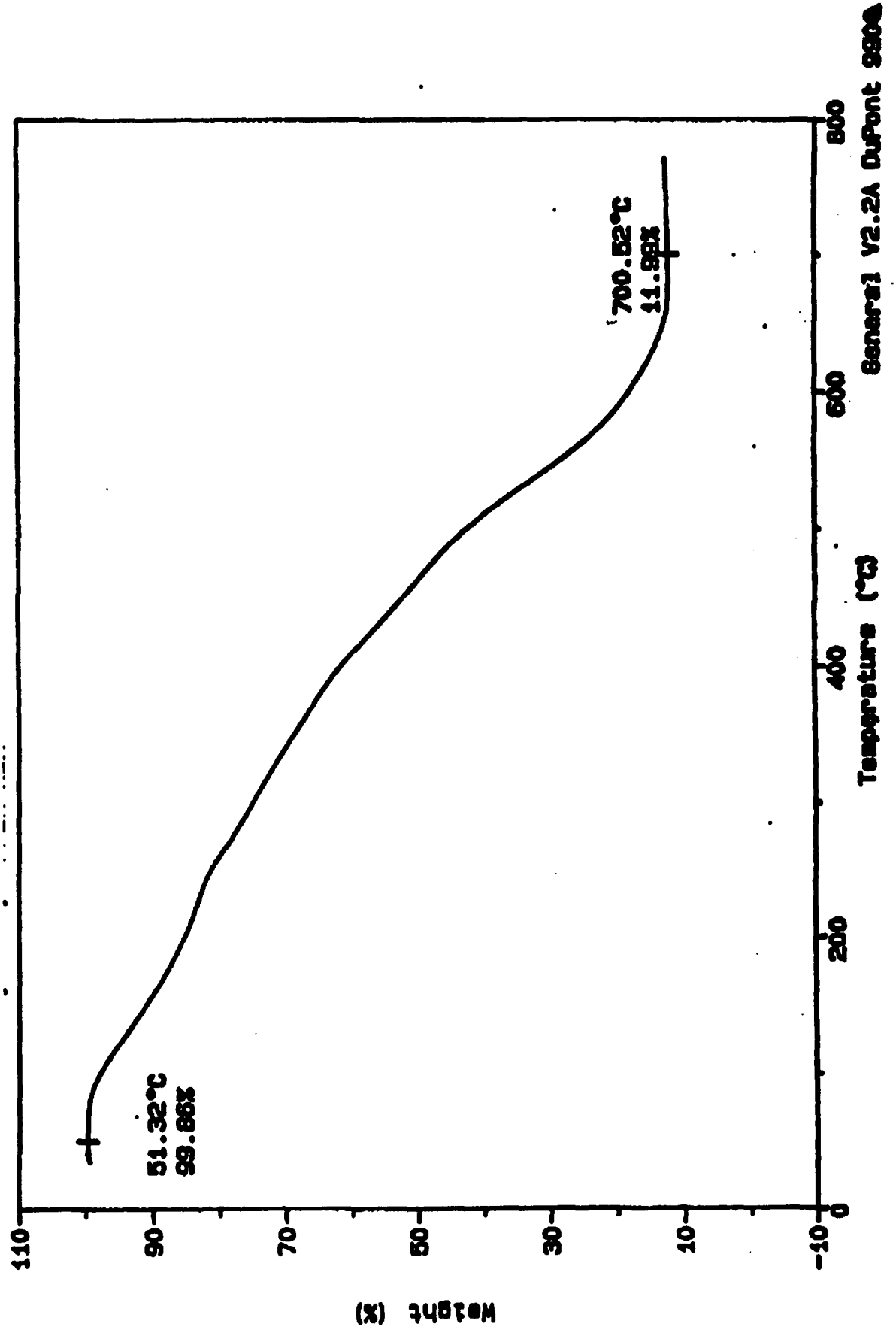

Figure 12. TGA thermogram of polyaniline (70%)/poly(MMA-MSMA) composite.

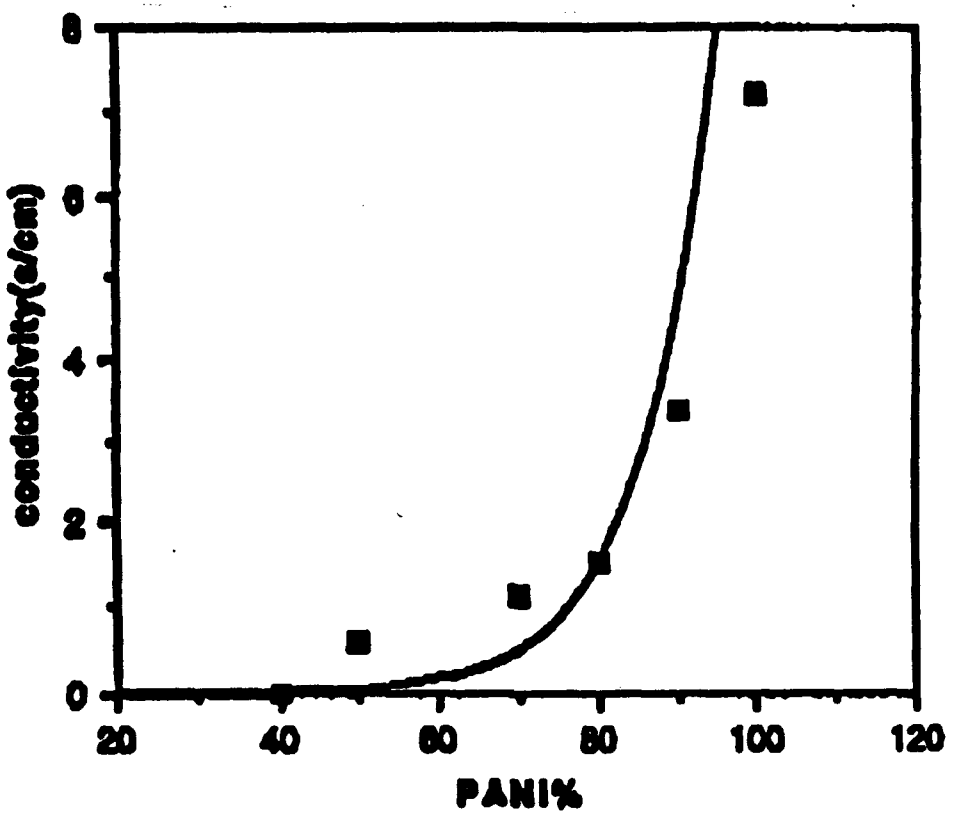

Figure 13. The effects of polyaniline concentration and thermal treatment on the conductivities of Polyaniline/ poly(MMA-MSMA) composites.

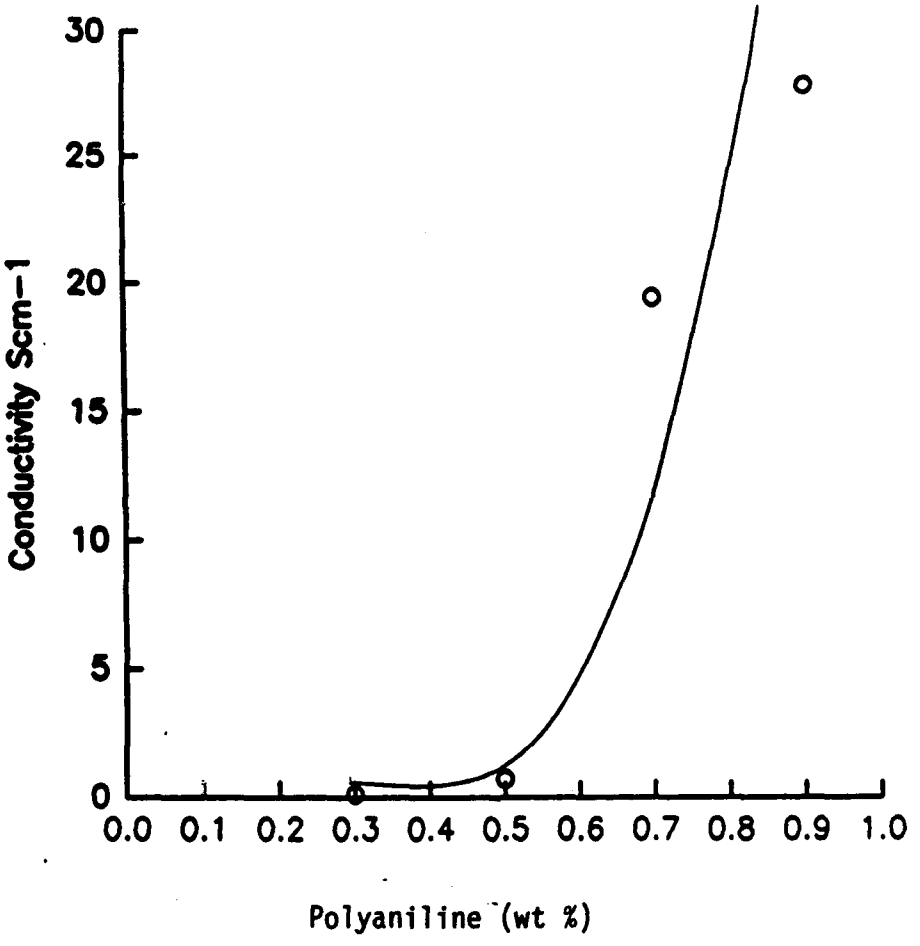

Figure 14. Conductivity vs % polyaniline of sol-gel composites on micro slide.

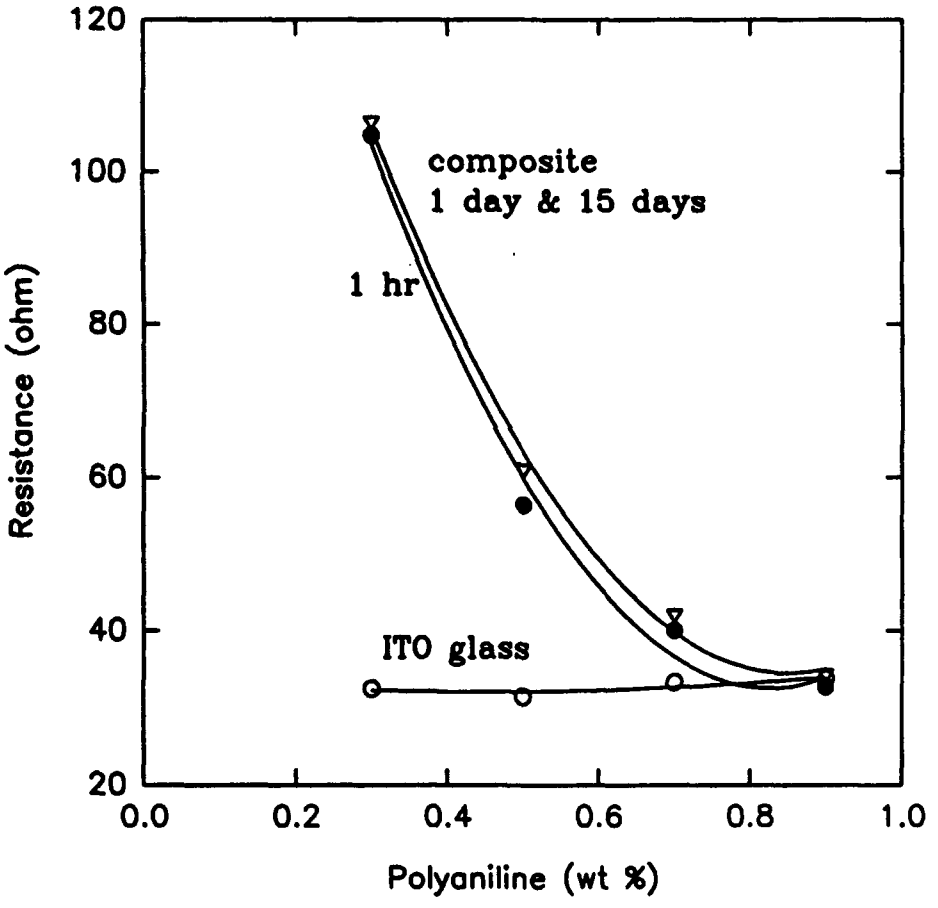

Figure 15. Resistance vs % polyaniline of sol-gel composites on ITO glass.